Theoretical Investigations on Carbocations. Structure and Stability of $C_3H_5^+$, $C_4H_9^+$ (2-Butyl Cation), $C_5H_5^+$, $C_6H_7^+$ (Protonated Benzene), and $C_7H_{11}^+$ (2-Norbornyl Cation)†

Hans-Joachim Köhler and Hans Lischka*

Contribution from the Arbeitsgruppe Quantenchemie, Sektion Chemie, Karl Marx Universität, DDR-701 Leipzig, German Democratic Republic, and Institut fur Theoretische Chemie und Strahlenchemie der Universität Wien, A-1090 Wien, Austria. *Received December 4, 1978*

Abstract: The title molecules have been investigated by ab initio methods including electron correlation and by the semiempirical MINDO/3 method. Electron correlation energies of the $C_3H_5^+$ system have been calculated explicitly by CEPA. In the other cases a complete CEPA calculation is no longer feasible and correlation effects have been estimated on the basis of pair-energy values. Experimental proton affinities of allene and propyne can be reproduced within experimental accuracy. In contrast, the calculated proton affinity of cyclopropene deviates significantly from the experimental value if, as it has been done in the literature, the cyclopropyl cation is assumed to be the protonated species. In order to resolve this discrepancy we have investigated the $C_3H_5^+$ energy hypersurface and looked for reasonable alternatives. As a solution of this problem we suggest that protonated cyclopropene has not been formed at all, but that ring opening has occurred yielding the 2-propenyl cation. An unusually large stabilization effect by polarization functions and by electron correlation has been observed for the square pyramidal form of $C_5H_5^+$ in relation to the planar cyclopentadienyl cation. This behavior is explained in terms of chemical bonding. In agreement with other theoretical investigations the σ complex of protonated benzene is found more stable than the π complex. The energy difference is estimated to lie between 1 and 6 kcal/mol, significantly less than obtained from double ζ SCF calculations. For the norbornyl cation system the classical structure is found less stable than the nonclassical one by about 8-13 kcal/mol. However, the edge-protonated stucture is nearly as stable as the nonclassical one. For an interpretation of experimental gas-phase data both of these structures should be considered.

I. Introduction

In the last decade experimental and theoretical evidence has increased strongly in the field of carbocation chemistry.[1] Experimental investigations may be divided into those which deal with solutions[2] (usually in superacid media) and into gas-phase experiments mainly performed by means of mass spectrometry[3] or ion cyclotron resonance[4] (ICR). Although especially the latter methods give very accurate thermodynamic data, one does not obtain direct information about the molecular structure. Thus, quantum mechanical calculations may be very useful: for many problems the molecules involved are small enough to allow ab initio calculations with sufficient accuracy. Since the theoretical calculations usually are performed for isolated molecules experimental gas-phase data are especially well suited for comparison. Only very few attempts have been made to include solvation effects into quantum chemical calculations.[5] A comparison of calculations for isolated molecules with experimental data from solution is much more difficult because one still does not know enough about solvation effects.

Basis-set effects and electron-correlation contributions to stability differences between open and cyclic cation structures are now well understood and documented.[6-8] In previous publications[8,9] we have investigated the possibilities of combining ab initio and semiempirical (MINDO/3) methods. Now we want to apply the experience we have obtained in these investigations to other cases for which open questions still exist. We shall also try to estimate correlation energy effects on the stability of larger molecules for which direct calculations are out of the question.

II. Methods of Calculation, Basis Sets and Geometries

At the ab initio level we start from an SCF calculation and compute electron correlation effects by the CEPA-PNO scheme.[10,11] The PNOs are computed from localized orbitals[12] and only the valence-shell correlation energy is calculated. As in ref 8b we take advantage of the fact that the interpair interactions between nonneighbor localized bonds are relatively small. Thus, they are computed at the IEPA level only. However, only the overall sum is given in the following tables under the heading of CEPA. In a previous work (ref 8b, Table IX) we have collected a large number of pair energy values from our calculations on carbocations and classified them with respect to the chemical bonds involved. One finds, in agreement with previous experience,[13] that the pair energy values for a certain type of bond are very well transferable from one molecule to another. For the systems investigated in ref 8b we could reproduce the correlation energy contributions to ΔE within 2-5 kcal/mol. Of course, we cannot guarantee such an accuracy in each case, but we think that the so estimated electron correlation effects provide a reliable basis for the calculation of the true stabilities of carbocations in cases where an explicit computation of correlation energies is no longer possible. In addition, the MINDO/3 method[14] and, in a few cases, the MNDO method[15] are used. Since we apply the same methods as in ref 8 and 9 we do not give more details here.

The thermodynamic quantities like $\Delta H°$ and $\Delta G°$ were computed from ΔE values given by CEPA and from zero-point energies and temperature dependence obtained from MINDO/3 results.[16] The calculations were performed within the rigid rotator/harmonic oscillator approximation. The way we combine ab initio and semiempirical data is a reasonable compromise in deducing thermodynamic data and has been applied successfully in a previous publication.[9]

The following basis sets are used for the calculations on carbocations: 7s3p on carbon and 3s on hydrogen (basis set no. 1); 7s3p1d on carbon and 3s on hydrogen (basis set no. 2); 7s3p1d on carbon and 3s1p on hydrogen (basis set no. 3). Basis sets 1 and 3 are identical with the basis sets 1 and 2 in ref 8b in which the contraction scheme and orbital exponents are also

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† Dedicated to Professor O. E. Polansky on the occasion of his 60th birthday.

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Table I. MINDO/3 Results: Heats of Formation (ΔH_f), Zero-Point Energies (ϵ_0), and Temperature Dependence of the Enthalpy and Free Energy (kcal/mol)[a]

molecule or cation	ΔH_f	ϵ_0[b]	$H_T^0 - H_0^0$ (T = 298.16 K)
propyne	34.96	36.46 (33.79)	3.12 (−14.58)[c]
allene	41.88	35.82 (33.31)	3.10 (−14.39)[c]
cyclopropene	59.29	36.67 (34.21)	2.70
benzene	28.43	63.58 (61.12)	3.56
hydrogen sulfide	−2.95	8.84 (9.18)	2.40 (−12.27)[c]
sulfhydronium	188.61	14.35	2.51 (−12.53)[c]
allyl (I)	221.98	43.37	3.21
2-propenyl (II)	213.52	41.55	3.66 (−15.90)[c]
corner-protonated cyclopropene, eclipsed (VIIb)	236.11	42.56	3.33
bridged protonated cyclopropene (VIII)	245.03	42.80	2.94
bridged protonated *trans*-2-butene (IX)	170.59	76.00	4.42
cyclopentadienyl, nonplanar singlet cation (XIb)	255.30	51.01	3.62
cyclopentadienyl, square-based pyramidal form (XII)	269.71	51.73	3.21
cyclohexadienyl (protonated benzene, open form) (XIII)	201.80	70.23	3.98
2-norbornyl, classical (XV)	214.17	104.77	4.47
edge-protonated nortricyclene (XVII)	216.90	105.13	4.07
H-bridged norbornene, exo form (XVIII)	218.78	104.60	4.28
H-bridged norbornene, endo form (XIX)	220.33	104.62	4.24
2-norbornyl, nonclassical asymmetric form (XX)	210.43	104.96	4.44

[a] All molecules and cations are minima on the MINDO/3 potential hypersurfaces. [b] The values given in parentheses are the experimental zero-point energies.[22] [c] Temperature dependence of the free energy ($G_T^0 - H_0^0$), T = 298.16 K (kcal/mol).

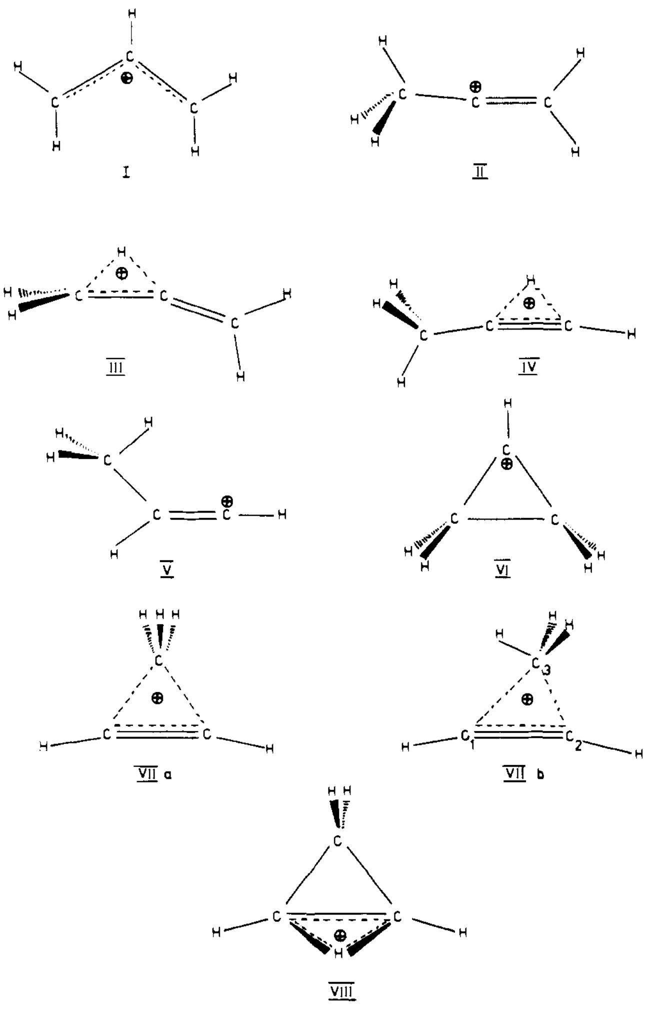

Figure 1. The $C_3H_5^+$ system.

Table II. Ab Initio Results (au) for Propyne, Allene, and Cyclopropene

	$-E_{SCF}$			$-E_{CEPA}$
molecule	basis set no. 1	basis set no. 2	basis set no. 3	basis set no. 2
propyne	115.731 35	115.775 55	115.787 00	116.155 27
allene	115.727 52	115.769 81	115.782 33	116.151 99
cyclopropene	115.662 70	115.728 68	115.740 92	116.117 78

given. For the calculations on H_2S and H_3S^+ we use a (11s7p2d/5s1p) Huzinaga basis set contracted to [752/31].

Most of the geometries for our ab initio calculations were taken from STO-3G results in the literature (see, e.g., ref 17). In cases where these data were not available we performed the geometry optimization (STO-3G basis) with the gradient program developed by Pulay.[18] The geometries are available on request.

III. Results and Discussion

A. $C_3H_5^+$. The $C_3H_5^+$ system has been investigated in detail at the SCF level by Radom et al.[19] Furthermore, MINDO/3 calculations for the interconversion of the allyl cation/cyclopropyl cation have been reported.[20] Experimental evidence has been obtained from ICR measurements of the protonation reaction of propyne, allene, and cyclopropene.[21] Since we shall finally give a different interpretation of the ICR experiment concerning the protonation of cyclopropene we have also investigated in detail the other two reactions and a number of $C_3H_5^+$ isomers. From the numerical agreement of our results with experiment in cases for which no discrepancies arise we want to draw conclusions for the controversial case as well. In Figure 1 the $C_3H_5^+$ structures investigated in this work are presented. Table I shows the pertinent MINDO/3 information (for all molecules treated in this paper) for the computation of ΔH values from ΔE_{CEPA} for the structures representing local minima on the MINDO/3 energy hypersurface. In Tables II and III we present our results for propyne, allene, and cyclopropene. The computed stabilities obtained from a 6-31G* basis and our CEPA results give good agreement with experiment. Only the MINDO/3 result for allene is unsatisfactory.

In Chart I our data for the protonation of propyne and allene by H_3S^+ are compared with experimental values. In connection with these protonation reactions we also optimized the py-

Table III. Relative Stabilities of Allene and Cyclopropene with Respect to Propyne

molecule	ΔE_{SCF}[a] basis set no. 1	basis set no. 2	6-31G*[b]	basis set no. 3	ΔE_{CEPA}[c]	$\Delta H°_{calcd}$[d]	$\Delta H°_{MINDO/3}$	$\Delta H°_{exptl}$[e]
propyne	0	0	0	0	0	0	0	0
allene	2.4	3.6	1.7	2.9	1.4	0.7	6.9	1.2
cyclopropene	43.1	29.4	25.4	28.9	23.0	22.8	24.3	21.8

[a] 1 au = 627.73 kcal/mol. [b] Reference 6. [c] SCF energy calculated with basis no. 3; correlation energy calculated with basis no. 2. See text. [d] On the basis of ϵ_0 and $H_T{}^0 - H_0{}^0$ from Table I. [e] Reference 23.

Table IV. Ab Initio Energies (au) for H_2S and H_3S^+ and Calculated Inversion Barrier (kcal/mol) for H_3S^+

molecule or cation	$-E_{SCF}$[a]	$-E_{CEPA}$[a]
hydrogen sulfide[b]	398.666 22	398.845 69
sulfhydronium, pyramidal[c]	398.948 61	399.129 86
sulfhydronium, planar[d]	398.897 02	399.081 24
inversion barrier	32.4 (32[e])	30.5

[a] Basis set: see section II. [b] Experimental geometry: r(S-H) = 1.328 Å, ∢HSH = 92.9°. [c] Calculated geometry: $r(\text{S-H})_{SCF}$ = 1.357 Å; $r(\text{S-H})_{CEPA}$ = 1.363 Å; $∢\text{HSH}_{SCF}$ = 96.2°; $∢\text{HSH}_{CEPA}$ = 94.5°. [d] Calculated geometry: $r(\text{S-H})_{SCF}$ = 1.324 Å; $r(\text{S-H})_{CEPA}$ = 1.342 Å. [e] Reference 24.

ramidal and planar structure of H_3S^+ at the CEPA level (see also Table IV). The inversion barrier at the SCF level agrees well with the results of Dixon and Marynick.[24] As in the case of PH_3,[25] the inversion barrier is modified only slightly by electron correlation effects. We obtain agreement between experimental and calculated values of proton affinities within the experimental error. The calculated $\Delta G°$ values for reactions 4 and 5 in Chart I differ from the experimental ones by 2-3 kcal/mol. On the other hand, we compute a value of 177 kcal/mol for the proton affinity of cyclopropene with respect to the cyclopropyl cation. This value differs by about 17 kcal/mol from the experimental one (194 kcal/mol) given in ref 21. Such a large discrepancy leads us to the supposition that the interpretation of the ICR experiment was incorrect. Our opinion is strengthened by the fact that equilibrium could not be obtained under the experimental conditions. In looking for alternatives to the cyclopropyl cation we investigated several other structures which were candidates for local minima or saddle points on the $C_3H_5^+$ energy hypersurface. As the basis of search we used the ab initio investigations of Radom et al.[19] and our own MINDO/3 calculations.

Chart I[e]

(1) $H_3S^+ = H_2S + H^+$
$\Delta E_{SCF} = 177.3$
$\Delta E_{CEPA} = 178.4$
$PA_{calcd}{}^a = 174.2$
$PA_{exptl} = 172.0 \pm 2^b$
173.9 ± 2^c
(2) $CH_3C^+{=}CH_2 = CH_3C{=}CH + H^+$
$\Delta E_{SCF} = 187.0$
$\Delta E_{CEPA} = 181.1$
$PA_{calcd}{}^a = 176.9$
$PA_{exptl}{}^d\ 174.0 \pm 3$
(3) $CH_3C^+{=}CH_2 = H_2C{=}C{=}CH_2 + H^+$
$\Delta E_{SCF} = 189.9$
$\Delta E_{CEPA} = 182.5$
$PA_{calcd}{}^a = 177.6$
$PA_{exptl}{}^d = 174.0 \pm 3$
(4) $CH_3C{\equiv}CH + H_3S^+ = CH_3C^+{=}CH_2 + H_2S$
$\Delta E_{SCF} = -1.0$
$\Delta E_{CEPA} = -2.7$
$\Delta H°_{calcd} = -2.7$
$\Delta G°_{calcd} = -4.2$
$\Delta G°_{exptl}{}^d = -2.1 \pm 0.1$
(5) $H_2C{=}C{=}CH_2 + H_3S^+ = CH_3C^+{=}CH_2 + H_2S$
$\Delta E_{SCF} = -1.3$
$\Delta E_{CEPA} = -4.1$
$\Delta H°_{calcd} = -3.4$
$\Delta G°_{calcd} = -5.1$
$\Delta G°_{exptl}{}^d = -2.0 \pm 0.1$

[a] $H°_{298.16} - H_0°$ for H^+ = 1.48 kcal/mol. [b] Reference 26a. [c] Reference 26b. [d] Reference 21. [e] All values in kcal/mol.

From the experience with our previous calculations[8b] we found that the p functions on hydrogen had a significant influence on the ΔE_{SCF} values only. The differences in correlation energy are almost unaffected. This behavior is illustrated in Table V. By addition of p functions on hydrogen the nonclassical ethyl cation and the edge-protonated cyclopropane are stabilized by ~4 kcal/mol with respect to the corresponding classical isomers (smaller stabilization effects of ~1 kcal/mol have been found by Hariharan et al.[6]); the energy difference between the 2-propyl cation and the corner-protonated cyclopropane is practically unaffected by addition of p functions on hydrogen even at the SCF level. Since the use of p functions increases the CEPA computation time drastically, we performed only the SCF calculations with inclusion of p functions (basis set no. 3) and omitted them in our CEPA calculations (basis set no. 2). Thus, the ΔE_{CEPA} value for the relative stabilities in Table VII is obtained by adding the ΔE_{SCF} values from basis set no. 3 in Table VI and the correlation energy correction (with CEPA) obtained from basis set no. 2.

In agreement with the 4-31G and 6-31G* calculations by Radom et al.[19] we also find from our MINDO/3 calculations that the cyclopropyl cation VI is a saddle point and opens in a disrotatory way to the allyl cation without activation energy. A small barrier of ~2.6 kcal/mol has been reported by Dewar[20] for the disrotatory ring opening from his MINDO/3 calculations. This barrier is due to an insufficient geometry optimization along the reaction path. For the protonated cyclopropene the MINDO/3 method shows two structures which are local minima. One structure is the corner-protonated cyclopropene VIIb. C_3 is positioned unsymmetrically with respect to the C_1C_2 bond ($r(C_1C_3)$ = 1.740 Å, $r(C_2C_3)$ = 1.573 Å, $r(C_1C_2)$ = 1.255 Å; see Figure 1). The second structure not yet considered in the literature is obtained by protonating the CC double bond in cyclopropene (structure VIII). Our MINDO/3 calculations for the reaction coordinate ($∢C_1C_2C_3$; see Figure 1) of the ring opening of VIIb give an energy barrier of 2 kcal/mol. Finally, the 2-propenyl cation is obtained. In the same way we find that structure VIII rearranges directly to the allyl cation with an energy barrier of 0.2 kcal/mol. This energy barrier is lower than the zero-point energy of the normal mode of VIII in the direction of the reaction path.

Besides structures VIIb and VIII we find local minima on the MINDO/3 energy hypersurface only for the allyl cation I and the 2-propenyl cation II. However, the relative stabilities of the latter two structures are given in the wrong order by MINDO/3. The structures of types III, IV, and V computed by MINDO/3 do not represent stationary points; structure VIIa is the saddle point for the interconversion of VIIb into its symmetric equivalent, and VI is the saddle point for the stereomutation of the allyl cation as already discussed above.

Table V. Ab Initio Energies (au) and Relative Stabilities (kcal/mol) for the $C_2H_5^+$ and $C_3H_7^+$ Isomers

cation	$-E_{SCF}$ basis set no. 2	$-E_{CEPA}$ basis set no. 2	ΔE_{SCF}		ΔE_{CEPA}	
			basis set no. 2	basis set no. 3[a]	basis set no. 2	basis set no. 3[a]
ethyl, classical	78.237 57	78.488 78	0	0	0	0
ethyl, nonclassical	78.234 03	78.494 27	2.22	−1.74	−3.45	−7.33
2-propyl	117.272 58	117.659 06	0	0	0	0
edge-protonated cyclopropane	117.237 08	117.648 67	22.28	19.20	6.52	2.49
corner-protonated cyclopropane	117.246 51	117.647 59	16.37	16.79	7.20	7.52

[a] Results from ref 8b.

Table VI. Energies (au) for $C_3H_5^+$ Isomers

cation	$-E_{SCF}$			$-E_{CEPA}$
	basis set no. 1	basis set no. 2	basis set no. 3	basis set no. 2
allyl (I)	116.045 77	116.093 55	116.109 71	116.461 71
2-propenyl (II)	116.024 60	116.068 41	116.084 84	116.438 71
bridged protonated allene (III)	115.982 04	116.036 52	116.060 56	116.415 26
H-bridged propenyl (IV)	115.971 70	116.033 26	116.058 29	116.413 09
1-propenyl (V)	115.998 65	116.042 89	116.058 61	116.410 55
cyclopropyl (VI)	115.965 05	116.028 14	116.044 38	116.392 62
corner-protonated cyclopropene, staggered (VIIa)	115.972 00	116.018 36	116.033 96	116.392 73
bridged protonated cyclopropene[a] (VIII)	115.914 20	115.992 85	116.016 78	116.380 68

[a] STO-3G energy = −114.711 66 au (this work).

Table VII. Relative Stabilities (kcal/mol) for the $C_3H_5^+$ Isomers with Respect to the Allyl Cation I

cation	ΔE_{SCF}					$\Delta H°_{calcd}$			
	basis set no. 1	basis set no. 2	6-31G*[a]	basis set no. 3	ΔE_{CEPA}[b]	CEPA	MINDO/3	MNDO	$\Delta H°_{exptl}$[d]
allyl (I)	0	0	0	0	0	0	0	0	0
2-propenyl (II)	13.3	15.8	16.7	15.6	14.3	12.9	−8.5	18.6	11
bridged protonated allene	40.0	35.8	34.0	30.9	24.2		c	c	
H-bridged propenyl (IV)	46.5	37.9	32.2	32.3	25.0		c	c	
1-propenyl (V)	29.6	31.8	32.5	32.1	32.4		c	30.8	
cyclopropyl (VI)	50.7	41.1	39.2	41.0	36.4		15.7	36.8	(12?)
corner-protonated cyclopropene staggered (VIIa)	46.3	47.2	42.6	47.6	37.9		14.1	57.9	
bridged protonated cyclopropene (VIII)	60.9	63.2		58.3	46.0		23.1	71.2	

[a] Reference 19. [b] SCF energy calculated with basis set no. 3; correlation energy calculated with basis set no. 2. See text. [c] No stationary point on the MINDO/3 or MNDO energy hypersurface. [d] Reference 21.

We recalculated the ring opening of structures VIIa and VIII with the STO-3G basis. Both structures are only stable with respect to geometry deformations by imposing symmetry restrictions. In both cases removing these restrictions led to ring opening without an energy barrier. We also performed SCF calculations with basis set no. 1 for the local minima VIIb and VIII and the corresponding saddle points obtained by MINDO/3. We could not confirm the existence of local minima for VIIb and VIII computed at the MINDO/3 level; i.e., we found that the ab initio SCF energies for the MINDO/3 saddle point geometries lie significantly lower than the energies of the MINDO/3 minimum geometries. Thus, from our ab initio calculations we do not expect that a local minimum for a protonated cyclopropene structure exists. However, since we have only performed STO-3G and 7s3p basis computations we cannot completely rule out the existence of such a minimum. Still, our MINDO/3 calculations show that if there is some local minimum (structures VIIb or VIII) the energy barrier for ring opening will not exceed 1-2 kcal/mol, enabling easy formation of the 2-propenyl and allyl cations.

Our view of the situation for the protonation of cyclopropene is presented graphically in Figure 2. The most favorable approach of a proton will probably be the one toward the CH_2 group in cyclopropene. As we have discussed in the preceding paragraph the ring opens very easily and rearranges via IV to the 2-propenyl cation. In agreement with the results of ref 19 we do not expect the 1-propenyl cation to be a stationary point on the energy hypersurface. The energy barrier for the hydride shift from II → III → I is decreased to about 10 kcal/mol by correlation effects. The calculated enthalpy difference of 12.9 kcal/mol between I and II is in good agreement with the experimental value of 11 kcal/mol.

Let us now return to the experimental proton affinities. We have shown above that the proton affinity of cyclopropene with respect to a hypothetical cyclopropyl cation is in serious disagreement with our results. However, if one looks at the scheme in Figure 2 one comes quite naturally to the conclusion that the protonated species formed is not the cyclopropyl cation but the 2-propenyl cation. Under these conditions we obtain 199.7 kcal/mol for the proton affinity of cyclopropene with respect to the 2-propenyl cation, which is in reasonable agreement with

Table VIII. Total Energies (au) and Relative Stabilities (kcal/mol) for the $C_4H_9^+$, $C_5H_5^+$, and $C_6H_7^+$ Isomers

	$-E_{SCF}$		ΔE_{SCF}					
cation	basis set no. 1	basis set no. 2	basis set no. 1	4-31G[c]	basis set no. 2	ΔE_{cor}^{csl} (CEPA)	ΔE_{CEPA}^{csl}	$\Delta H°$ (MINDO/3)
		STO-3G Geometry						
bridged protonated *trans*-2-butene (IX)[a]	156.193 45	156.271 79	0		0	0	0	
2-butyl (X)[b]	156.209 78	156.278 88	−10.2		−4.5	11	6	
					~−0.5[d]		10[d]	
		MINDO/3 Geometry						
bridged protonated *trans*-2-butene (IX)	156.182 46	156.261 68	0		0	0	0	0
2-butyl (X)	156.202 98	156.272 06	−12.9		−6.5	11	4	5.1
					~−2.5[d]		8[d]	
		STO-3G Geometry						
cyclopentadienyl, planar singlet (XIa)	191.656 97	191.745 62	0	0	0	0	0	0
cyclopentadienyl, square-based pyramidal form (XII)	191.551 54	191.693 65	66.2	53.8	32.6	−24[f]	9	14.4
cyclohexadienyl, open form (XIII)	230.722 47	230.758 99[e]	0	0	0	0	0	
cyclohexadienyl, bridged form (XIV)	230.688 76	230.733 51[e]	21.2	20.6	16.0	−11	5	
					~12.0[d]		1[d]	
		MINDO/3 Geometry						
cyclohexadienyl, open form (XIII)	230.723 80	230.760 47[e]	0		0	0	0	0
cyclohexadienyl, bridged form (XIV)	230.681 61	230.727 05[e]	26.5		21.0	−11	10	8.0
					~17.0[d]		6[d]	

[a] STO-3G energy = −154.590 50 au (this work). [b] STO-3G energy = −154.611 99 au (this work). [c] References 17, 29, and 32, respectively. [d] Energy difference with inclusion of the estimated effect of the p functions on the bridging hydrogen atom. [e] Only d functions on the atoms 1 and 2; see Figure 3. [f] In estimating the correlation energy for the planar cyclopentadienyl cation results from the allyl cation have been used in addition to the other parameters of ref 8b.

the experimental value of 194 ± 3 kcal/mol.[21] Moreover, the experimental ΔH_f of 238 kcal/mol for the protonated species agrees very well with the experimental ΔH_f of 237 kcal/mol for the 2-propenyl cation.

From our scheme in Figure 2 we would also expect the formation of the allyl cation via structure VIII to some extent. However, the calculated proton affinity of 212.6 kcal/mol is relatively far off the experimental value.

For comparison we give MNDO results also in Table VII. The relative order of I vs. II is correctly reproduced in contrast to the MINDO/3 results. The structures VIIa and VIII are strongly decreased in stability in comparison to the CEPA results and are found to be saddle points. We have also checked the applicability of the MNDO method for the carbocation systems $C_2H_3^+$, $C_2H_5^+$, and $C_3H_7^+$. In agreement with the calculations performed by Thiel[27] and in contrast to CEPA and MINDO/3 results we find the stability of the classical structures largely exaggerated. For example, the classical structure of the ethyl cation is more stable than the nonclassical one by 15.1 kcal/mol. The edge-protonated cyclopropane lies 32.3 kcal/mol above the isopropyl cation and is not a minimum but a saddle point. These results lead us to the conclusion that the MNDO method in its present form is not adequate for the description of carbocations.

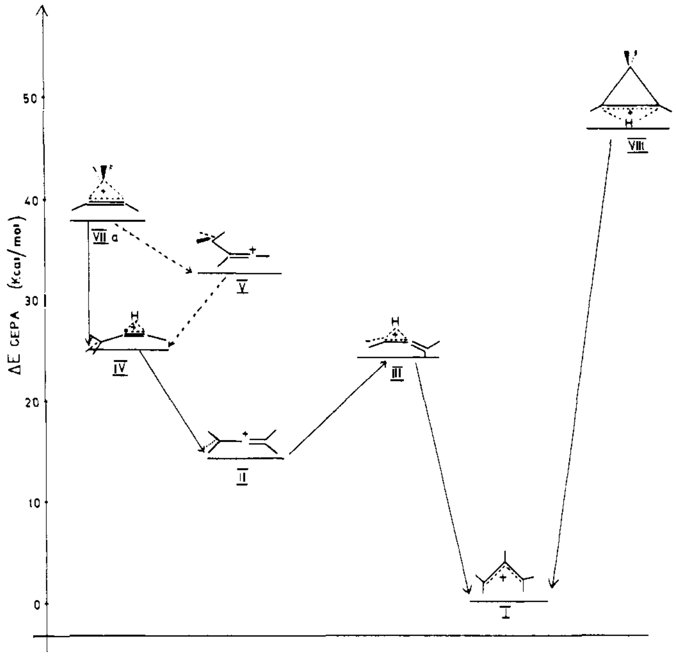

Figure 2. Reaction profile for the interconversion of the $C_3H_5^+$ isomers.

B. $C_4H_9^+$. The geometries of the 2-butyl cation X and the related bridged structure IX have been optimized at the STO-3G and MINDO/3 level (see Figure 3). Total energies and relative stabilities are given in Table VIII. We performed SCF calculations with basis sets no. 1 and 2 only. From calculations on similar systems we have learned (see Table V) that by addition of p functions on hydrogen the bridged structure is stabilized by ~4 kcal/mol with respect to the classical structure. This correction is implemented in Table VIII. As we have already indicated in section II, we are able to give relatively reliable estimates of correlation energy effects from our pair energy parameters (shown in Table IX of ref 8b) for systems which show a similar type of bonding. By simply classifying the interactions between localized bonds in the $C_4H_9^+$ system and using the appropriate pair energies we compute a stabilizing effect of electron correlation at the CEPA level of approximately 11 kcal/mol for the bridged system. This is somewhat larger than the calculated stabilization for the $C_2H_5^+$ system (8 kcal/mol with our pair energy parameters). The stability differences between IX and X obtained with the STO-3G and MINDO/3 geometries, respectively, agree quite well. As a final estimate we obtain the bridged structure IX to be more stable than the open structure X by 8–10 kcal/mol. Experimental information is available

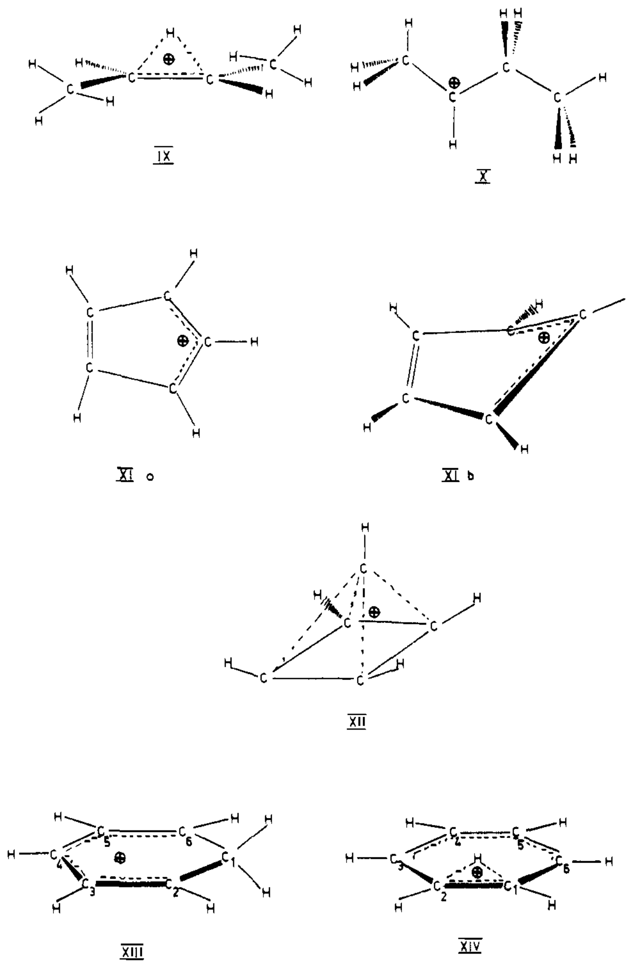

Figure 3. The systems $C_4H_9^+$, $C_5H_5^+$, and $C_6H_7^+$.

for superacid media only.[2b,28] In this case the experimental data are explained by a degenerate 2,3-hydride shift for the 2-butyl cation. Solvent effects are certainly responsible for the different order of stability between our theoretical results for the gas phase and the results in solution.

C. $(CH)_5^+$. The $(CH)_5^+$ system has been investigated both theoretically[29-32] and experimentally.[33-36] We restrict ourselves to the singlet state of the cyclopentadienyl cation structure XI and to the square pyramidal form XII first proposed by Stohrer and Hoffmann[29] (see Figure 3). The MINDO/3 results[32] show that the nonplanar cyclopentadienyl cation XIb is more stable than the planar one (XIa) by 0.7 kcal/mol (refined value, this work) only. Therefore, we restricted our ab initio investigations to the planar form XIa. Both the 4-31G basis and our basis no. 1 (see Table VIII) show the square pyramidal form to be highly unstable (55-66 kcal/mol). Since one may interpret structure XII as being composed from a cyclobutadiene and a CH^+ moiety three electron pair bonds closely spaced are responsible for the bonding between the two subunits. Thus one would expect a large effect of d functions on stability.[30] Indeed, with basis set no. 2 a stabilizing effect of 33 kcal/mol is observed. The close packing of orbitals in space has, of course, its consequences on electron correlation effects also. Estimating electron correlation energy differences in the same way as described for the $C_4H_9^+$ system increases the stability of XII again by ~24 kcal/mol. As a whole we find a tremendous change going from calculations of approximately double ζ quality to (estimated) results including correlation effects.

The square pyramidal form has been reported to exist in solution.[35,36] In view of this fact structure XII lies unrealistically high above XI in energy when 4-31G and 7s3p basis sets are used. Inclusion of d functions and electron correlation effects leads to a much more satisfactory picture.

D. $C_6H_7^+$. Mass spectroscopic and ICR measurements in the gas phase as well as investigations in solution are available for the protonated benzene system.[37] The theoretical investigations[38] concentrate on the comparison of the classical σ complex XIII with the bridged π complex XIV (see Figure 3). We start again from STO-3G calculations in the literature[38b] and from our own MINDO/3 calculations. Only a partial geometry optimization has been performed for structures XIII and XIV at the STO-3G level.[38b] In Table VIII stabilities calculated from STO-3G and MINDO/3 geometries are reported. Our ΔE_{SCF} with basis no. 1 (21.2 kcal/mol) agrees well with the 4-31G result of 20.6 kcal/mol.

It is of course highly desirable to have available SCF calculations with inclusion of polarization functions.[38d] Our computer capacity did not allow us to use basis sets with d functions placed on each carbon atom. As a compromise we added a set of d functions on the carbon atoms C_1 and C_2 (see Figure 3). The basis set effects are of the expected magnitude. In our approach of estimating correlation energy effects the comparison of structures XIII and XIV parallels the one for IX and X. Thus we compute again a contribution of ~10 kcal/mol in favor of the bridged structure. Another estimate of the correlation effect in $C_6H_7^+$ by Heidrich et al.[39] based on the semiempirical EPCE-F2σ model of Pamuk and Sinanoglu gives ~9 kcal/mol. Depending on the geometries used we find the σ complex XIII to be more stable than the π complex by 1-6 kcal/mol, which is a remarkable change with respect to the original 20 kcal/mol obtained from basis set no. 1. The π complex is a saddle point for hydrogen migration. The low energy barrier is in agreement with the relative ease which is found experimentally for this migration process.[37a] The MINDO/3 method predicts an energy difference of 8 kcal/mol. Taking a standard geometry for benzene (r(CC) = 1.40 Å, r(CH) = 1.08 Å)[38b] we compute the proton affinity of benzene at the SCF level with basis set no. 2 (but see footnote e in Table VIII). Since we could not check whether our pair energies in Table IX of ref 8b are also applicable to aromatic systems we did not attempt an estimate of the correlation energy of benzene. We obtain for the protonation process of benzene a ΔE_{SCF} value of 185.8 kcal/mol, leading to a proton affinity of 180.2 kcal/mol. A ΔE_{SCF} value of 189.1 kcal/mol has been obtained by Ermler et al.[38d] with a much larger basis set including polarization functions on all atoms. Our value is in very good agreement with this result. The experimental value is 183 kcal/mol.[26a,40]

E. $C_7H_{11}^+$. The controversies regarding the structure of the 2-norbornyl cation system are well-known.[41,42] Theoretical[43-45] and experimental investigations in superacid media[46] and in the gas phase[47] now tend to favor the bridged structure XVI over the classical structure XV (see Figure 4). We proceed the same way as we did in the case of protonated benzene. In Tables IX and X energies and stabilities obtained from STO-3G and MINDO/3 geometries are compared. A balance use of d functions is more complicated here since different types of structures are involved; as a reference structure we take the classical cation XV. Discussing the relative stabilities of XV, XVI, and XVII a basis set with d functions on C_1, C_2, and C_6 is used (see Figure 4). When we want to compute the relative stability of XVIII and XIX with respect to XV, d sets are added to C_2 and C_3. The case of the stability of XX is treated by the use of a basis with d functions on C_1, C_2, and C_7. MINDO/3 calculations[45] as well as STO-3G and 4-31G calculations[43] predict the classical structure XV to be more stable than the nonclassical cation XVI. The energy differences are rather small, ranging from 0.2 to 5.2 kcal/mol. However, somewhat unexpectedly, from MINDO/3 computations one

Table IX. Total Energies (au) for the 2-Norbornyl Cation Isomers XV-XX

cation	$-E_{SCF}$ basis set no. 1	$-E_{SCF}$ basis set no. 2
2-norbornyl, classical (XV)		
STO-3G geometry[a]	270.851 00	
MINDO/3 geometry	270.839 56	270.895 84[d] 270.876 55[e] 270.895 31[f]
2-norbornyl, nonclassical (XVI)		
STO-3G geometry[b]	270.849 66	
MINDO/3 geometry	270.829 66	270.890 49[d]
edge-protonated nortricyclene (XVII)		
STO-3G geometry[c]	270.823 33	
MINDO/3 geometry	270.811 51	270.878 41[d]
H-bridged norbornene, exo form (XVIII)		
MINDO/3 geometry	270.805 03	270.851 04[e]
H-bridged norbornene, endo form (XIX)		
MINDO/3 geometry	270.795 12	270.841 46[e]
2-norbornyl, nonclassical asymmetric form (XX)	270.801 89	270.865 16[f]

[a] STO-3G energy = −268.052 52 au (this work). [b] STO-3G energy = −268.044 92 au (this work). [c] STO-3G energy = −268.028 37 au (this work). [d] d functions on atoms 1, 2, and 6 only; see Figure 4. [e] d functions on atoms 2 and 3 only; see Figure 4. [f] d functions on atoms 1, 2, and 7 only; see Figure 4.

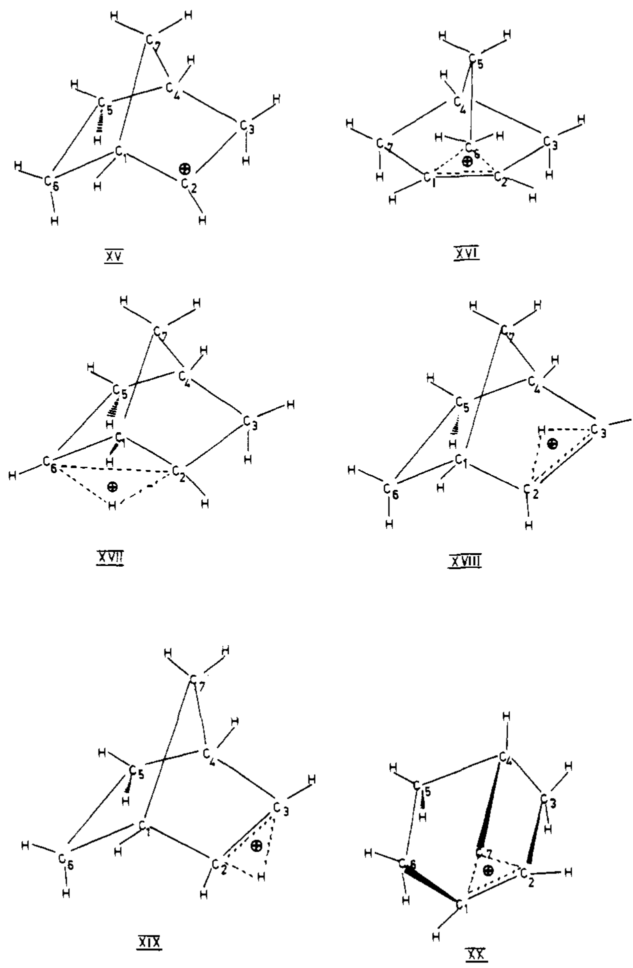

Figure 4. The 2-norbornyl cation system.

finds structure XX even more stable than XV. The edge-protonated nortricyclene XVII has not been treated by ab initio methods so far. The MINDO/3 results indicate, however, that this structure should not be overlooked in a search for the most stable geometry.

The effect of polarization functions and the influence of electron correlation on the stability difference between XV and XVI have been discussed qualitatively by Goetz et al.[43] These authors come to the conclusion that the nonclassical cation is more stable than the classical structure. The edge-protonated structure XVII is analogous to the edge-protonated cyclopropane. The changes in stability given in Table X reflect this analogy. The CEPA correlation energy contributions are estimated in the same way as for $C_4H_9^+$, $(CH)_5^+$, and $C_6H_7^+$. As in the case of protonated cyclopropane structures[8b] the edge-protonated form XVII is stabilized significantly with respect to the other structures. Our estimate of the correlation energy effect shows not only that the nonclassical structure XVI is more stable than XV but also that the edge-protonated nortricyclene XVII has approximately the same stability. So far, the investigations in the literature were mainly concerned with the distinction of structures XV and XVI. Our calculations show that the problem is even more complicated. At least for the gas phase it seems quite likely that the classical structure does not correspond to a local minimum. However, both bridged structures XVI and XVII may represent local minima and have to be taken into account. As one can see from Table

Table X. Relative Energies (kcal/mol) for the 2-Norbornyl Cation Isomers XV-XX

cation	ΔE_{SCF} basis set no. 1	ΔE_{SCF} basis set no. 2	ΔE_{cor}^{est} (CEPA)	ΔE_{CEPA}^{est}	$\Delta H°$ (MINDO/3)
	STO-3G Geometries				
2-norbornyl, classical (XV)	0		0	0	
2-norbornyl, nonclassical (XVI)	0.8	~−2	−11	−13	
edge-protonated nortricyclene (XVII)	17.4	~7	−15	−8	
	MINDO/3 Geometries				
2-norbornyl, classical (XV)	0	0	0	0	0
2-norbornyl, nonclassical (XVI)	6.2	3.4[a]	−11[e]	−8[a]	1.9
edge-protonated nortricyclene (XVII)	17.6	10.9;[a] ~7[d]	−15	−4;[a] −8[a,d]	2.7
H-bridged norbornene, exo form (XVIII)	21.7	16.0[b]	−11	5[b]	4.6
H-bridged norbornene, endo form (XIX)	27.9	22.0[b]	−11	11[b]	6.2
2-norbornyl, nonclassical asymmetric form (XX)	23.6	18.9[c]	−11	8[c]	−3.7

[a] Only d functions on atoms 1, 2, and 6; see Figure 4. [b] Only d functions on atoms 2 and 3; see Figure 4. [c] Only d functions on atoms 1, 2, and 7; see Figure 4. [d] Energy difference with inclusion of the estimated effect of the p functions on the bridging hydrogen atom. [e] See also ref 39.

1, zero-point energies and $H_T^0 - H_0^0$ values are remarkably constant for all of the 2-norbornyl cation isomers.

We have also performed calculations for structure XX, which is the most stable one given by MINDO/3. We confirm the STO-3G computations by Dewar et al.[45] with our basis set no. 1. The influence of d functions is relatively small. The effect of the correlation energy is not large enough to make structure XX more stable than XV. The exo and endo forms of the H-bridged norbornyl cations (XVIII and XIX) are obtained less stable in relation to XV with our ab initio methods than with MINDO/3.

IV. Conclusions

We have shown that using STO-3G optimized geometries experimental proton affinities and ΔG values for hydrocarbon systems can be reproduced with an accuracy of a few kilocalories per mole. Other examples have been published previously.[9] We have used this fact to propose a scheme for the protonation of cyclopropene which differs from the original interpretation of the ICR experiment. An enormous influence of polarization functions and of electron correlation has been found for the stability of the square pyramidal structure of $(CH)_5^+$. With a basis of approximately double ζ quality one finds the planar singlet cyclopentadienyl cation more stable than the square pyramidal form by ~66 kcal/mol. Including polarization functions and estimating correlation effects this difference is reduced to about 9 kcal/mol.

Our calculations on the 2-norbornyl cation system show the energetic preference of nonclassical structures. This is in agreement with the current trends of experimental as well as theoretical investigations. However, we want to stress that in addition to the nonclassical 2-norbornyl cation XVI one should also consider the edge-protonated nortricyclene XVII. In our computations both structures are found to be of approximately equal stability.

Note Added in Proof. Recently, the 2-norbornyl cation system has been treated by G. Wenke and D. Lenoir [*Tetrahedron*, **35**, 489 (1979)] at the MINDO/3 and STO-3G levels. Because of our complete geometry optimization we obtain somewhat lower total STO-3G energies than Wenke and Lenoir do. However, their energy differences are in good agreement with our results.

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